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**PRESSURE OSCILLATIONS IN A
LIQUID PROPELLANT GUN—POSSIBLE
DEPENDENCE ON PROPELLANT BURNING RATE**

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JUNE 1992

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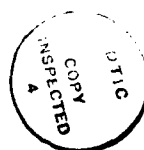
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13. ABSTRACT (Maximum 200 words) High frequency pressure oscillations have been observed in liquid propellant gun firing records, and modeling of the combustion process indicates that the oscillations are affected by the burning rate of the propellant. The HAN-based propellants have consisted of stoichiometric, aqueous mixtures of the nitrate salts of hydroxylamine (HAN) and an aliphatic amine (AAN). These mixtures decompose sequentially because HAN is less stable thermally than is the AAN. Combustion is obtained when the products of the HAN decomposition react with the molten AAN droplets. The nitrate salts of tertiary amines result in the smoothest and most rapid combustion, and thus triethanolammonium nitrate (TEAN) is the AAN salt used in the propellants LGP1845 and LGP1846. Attempting to further raise the burning rates of the propellant mixtures requires circumventing the sequential nature of the reactions. Decomposition of hydroxylamine in which alkyl groups have replaced hydrogen should be essentially concomitant with HAN but reactive organic fragments will be available sooner and such mixtures should burn faster. Using the nitrate salt of N,N-diethylhydroxylamine (DEHAN), a mixture containing 20% water was prepared. This propellant burns 17 times faster than LGP1846 and the combustion model indicates that the HAN-DEHAN mixture should essentially eliminate the observed pressure oscillations.				
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1. INTRODUCTION

Oscillations are almost always observed in chamber pressure records obtained from the firing of regenerative liquid propellant guns (LPGs). High-frequency oscillations appear in 30-mm and larger caliber guns (Pate and Magoon 1985; Mandzy et al. 1983; Magoon, Haberl, and Purtee 1989), usually cover a broad frequency range (Watson 1989), and are not affected to any significant extent by modifications in the injector design (Watson, Knapton and Boyer 1989); although devices such as jet flow dispersers can reduce the amplitude of low-frequency oscillations (DeSpirito et al. 1991). Since the oscillations extend to fairly high frequencies, they can excite resonances in various gun components. Although no difficulties have been experienced to date that can be attributed to these pressure oscillations, the potential for damage exists and serious questions have been raised about increased gun tube erosion and deleterious effects on payloads sensitive to mechanical vibration.

The extent to which the higher frequency oscillations are unaffected by gun geometry raises the possibility that they are associated with a fundamental property of the combustion of the propellants used. The HAN-based propellants, in general, are aqueous, homogeneous mixtures of hydroxylammonium nitrate (HAN) and a fuel, usually the nitrate salt of an aliphatic amine. This second component is required because HAN is too oxygen-rich to serve as an efficient monopropellant. The rate at which gas is generated is closely related to the molecular structure of the fuel component—the nitrate salts of tertiary aliphatic amines producing the fastest and most uniform rate of gas evolution of all of the fuels studied to date (Klein 1983). In all of the cases in which pressure oscillation was observed, the propellants employed were LGP1845 or LGP1846, both of which utilize the nitrate salt of triethanolamine (TEAN) as the tertiary amine fuel. The structural formulas of HAN and TEAN are shown in Figures 1a and 1b. Several features of the structures, notably, the ion-pairing between nitrate and the hydroxylammonium and triethanolammonium ions, and the OH groups of the triethanolammonium ion, are especially important and will be addressed in subsequent discussion. The mixtures contain just enough oxygen to produce N_2 , CO_2 stoichiometry so that the HAN:TEAN weight ratio is 3.17. Energy content is strongly dependent on the amount of water present and LGP1845, containing 16.8% water, has an impetus of 934.2 J/g and a flame temperature of 2,592 K. The less energetic LGP1846 contains 20.0% water, resulting in an impetus of 900.8 J/g and a flame temperature of 2,476 K. Both impetus and flame temperature values are computed for a loading density of 0.2 g/ml.

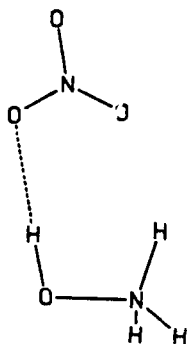


Figure 1a. Hydroxylammonium Nitrate (HAN).

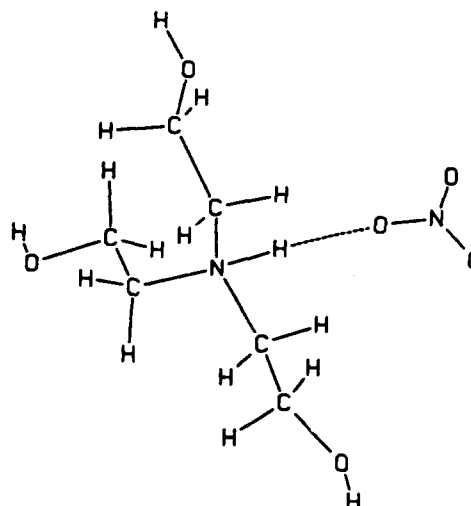


Figure 1b. Triethanolammonium Nitrate (TEAN).

The chemistry observed when reaction is initiated is sequential, the first reactions being decomposition of the HAN component of the mixture. Heat is released and gases are generated, leaving droplets of molten TEAN finely dispersed throughout the HAN decomposition gases. Ignition and combustion involves reaction of these gases and the TEAN droplets (Klein, to be published).

Recently, a two-dimensional model for the regenerative LPG has been developed specifically to examine the pressure oscillations (Coffee, to be published). The combustion chamber is idealized as a cylinder. Liquid propellant (LP) is injected in the form of droplets through an annulus in the left wall of the chamber. The droplets immediately ignite and burn according to a pressure-dependent surface regression rate of the form AP^B . The left wall can move, thus mimicking the motion of the pistons in an actual regenerative gun. The gun tube is another cylinder with a movable projectile at the right wall. Hot gas is generated near the injector annulus and flows into the gun tube, accelerating the projectile. The full two-phase Navier-Stokes equations are solved, including a two-equation turbulence model. Appropriate values for injection rate and droplet size are obtained from a lumped parameter gun code which has been extensively validated against experiment.

As the liquid is injected, it begins to burn and raises the pressure locally because the inertia of the gas keeps the high pressure region from immediately decaying. This causes the combustion rate to increase because it is pressure dependent. Eventually, the gas inertia is overcome and the high-density gas moves away from the injection region. The resulting pressure wave can reflect from a wall and return to the

injector region. If the pressure wave happens to return while rapid combustion is still in progress, it will further raise the combustion rate and increase the magnitude of the high-pressure region. Eventually, waves with very high peak pressures will be generated, their frequency probably matching some acoustic mode of the chamber.

Figure 2 compares the chamber pressure obtained experimentally from a 155-mm gun firing with the chamber pressure calculated using the model. The model pressure has been shifted downward 150 MPa to permit comparison. Oscillations are seen in the model at about the same time after the start of propellant injection as are observed experimentally, but the oscillations generated by the model die out more quickly. The magnitude of the model-generated oscillations is close to those experimentally observed. The dominant frequencies generated by the oscillations in both cases were determined as a function of time. The Fourier transforms of the experimental data and the model (for a time window 1 ms wide) 11 ms after the start of the oscillations are shown in Figure 3. Figure 4 shows the Fourier transforms 3 ms later. Both sets of data show a complicated frequency pattern, the experimental data containing a more complex, high-frequency structure. The third radial mode (around 11 kHz) is excited primarily in the model because the liquid is injected about one third of the way from the centerline to the wall. Disagreement between experimental and model data may be due either to the simplified geometry of the chamber in the model, or to major simplifications in the injection and combustion processes. In spite of these differences, the model captures the qualitative behavior of the system.

Oscillations in the model may be reduced or eliminated by adjusting the surface regression rate, AP^B . If the exponent B is small, combustion rate is insensitive to pressure and the small, initial pressure waves will not be reinforced because they have only a negligible effect on the burning rate. If, on the other hand, the pressure exponent is larger than one, pressure waves will be reinforced and oscillations are likely (Strahle 1972). Recent measurements indicate that the pressure exponent is near two for LGP1846 at pressures between 80 and 200 MPa (Oberle and Wren 1990). Another possible method for controlling pressure oscillations is to increase the pre-exponential factor A in AP^B which will increase the burning rate of the propellant. If the burning rate is fast enough, the liquid will combust almost as rapidly as it is injected. Since there will be essentially no liquid accumulation, initial pressure waves cannot be reinforced. The model predicts a decrease in pressure oscillations if either B is decreased or A is increased.

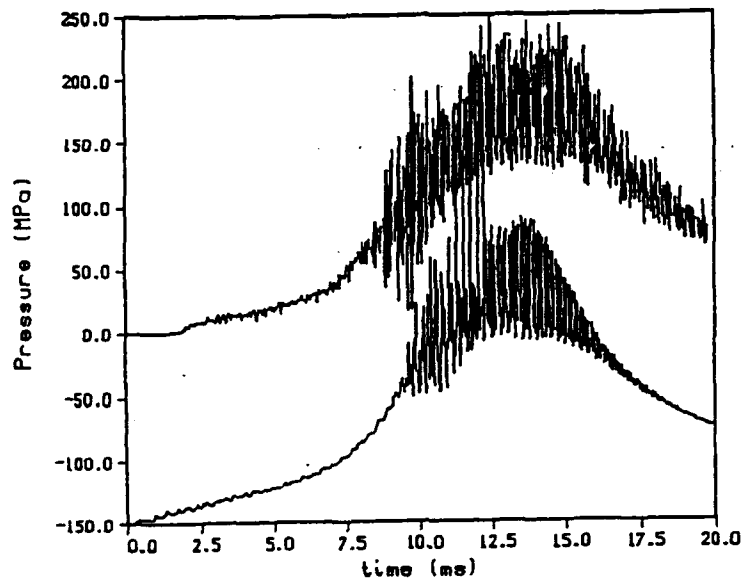


Figure 2. Experimental Chamber Pressure From a 155-mm Gun, Round 65 (Top).
Model Chamber Pressure at the Wall (Bottom).

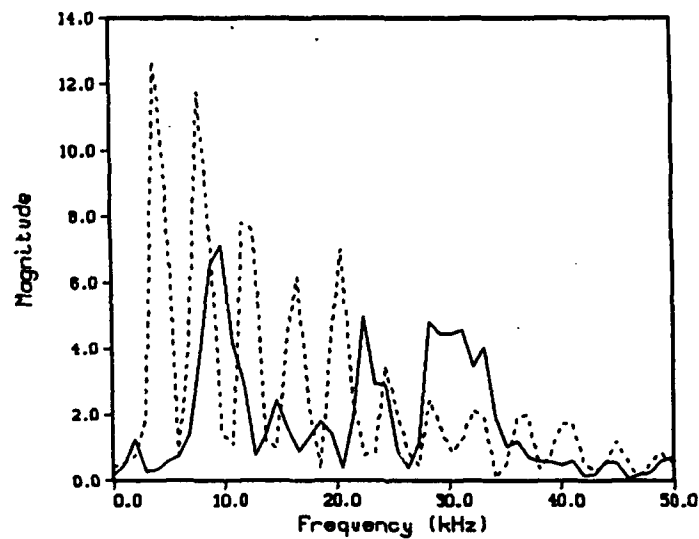


Figure 3. Fourier Transforms - 11-12 ms. Experiment (Line). Model (Dot).

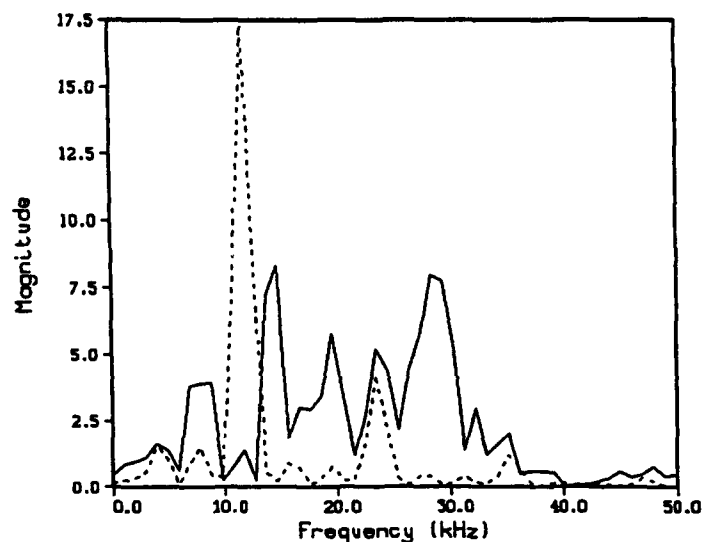


Figure 4. Fourier Transforms - 14-15 ms. Experiment (Line). Model (Dot).

The combustion of LGP1846 involves reaction of molten TEAN droplets with the gaseous decomposition products of HAN and reaction rate should be strongly pressure dependent. Although quantitative estimation of the pressure exponent requires a detailed, and as yet unavailable knowledge of the reaction mechanism, a value near two for B is not surprising. Reduction of pressure oscillations by reducing the value of B thus appears futile for HAN-amine nitrate mixtures and attempts to increase burning rate by increasing the value of the pre-exponential term were addressed. Since the tertiary amine nitrates produce the highest burning rates of the HAN-fuel mixtures, thought was given to creation of another class of aqueous homogeneous gun propellants. A number of physical and chemical properties must be considered in selecting propellant components (Klein 1988) and HAN is easily the oxidizer of choice for such mixtures. Because the reactions of the HAN-fuel mixtures are sequential with HAN reacting first, the use of an alkyl hydroxylamine could introduce reactive organic fragments into the gas phase sooner than is obtained with HAN-TEAN mixtures, and thus increase the burning rate of the propellant. An aqueous mixture of the nitrate salt of a dialkylhydroxylamine and HAN were thus considered as a potential propellant. This report addresses the preparation of such a mixture and some of the preliminary data obtained as part of the evaluation of the mixture as a potential gun propellant.

2. EXPERIMENTAL

The HAN structural formula presented in Figure 1a shows the hydrogen atoms attached to nitrogen, as well as the hydrogen of the OH group. Any of the hydrogen atoms can be replaced by an organic functional group. Ion-pairing between the nitrate and hydroxylammonium ions in HAN strongly influences the physical properties of the propellant mixture and primarily involves the hydrogen of the OH group (Klein and Wong 1987). It was thus considered prudent not to disturb this portion of the molecule. N,N-diethylhydroxylamine (DEHA), with the structural formula shown in Figure 5, is commercially available (Aldrich D9720-7)* at 97% purity. The compound was distilled (boiling range 129–131° C) immediately prior to use. The DEHA was converted to its nitrate salt (DEHAN) by dropwise addition at 0° C with vigorous stirring, to a 2-molar solution of nitric acid. Temperature should not exceed 5° C and nitric acid concentration must be no higher than 2M in order to avoid oxidation of the hydroxylamine to its corresponding nitron (Smith 1966), an undesirable side reaction. The dilute DEHAN solution thus obtained was concentrated to 93.64 weight-percent by water stripping at 50° C under vacuum. DEHAN at this concentration is a stable, homogeneous, yellow-brown, viscous liquid at room temperature.

HAN and TEAN form stoichiometric mixtures with a HAN:TEAN molar ratio of 7:



whereas, HAN and DEHAN require the following:



It is, therefore, possible to produce both binary and ternary HAN mixtures that will give N₂, CO₂, and water as sole combustion products. A set of such mixtures, each containing 20% water, were designed and their performance computed using the BLAKE thermochemical code (Freedman 1982). Results are presented in Table 1. Propellant 4600 is empirically formulated to be identical to LGP1846. The table shows that energy content increases as TEAN is replaced by DEHAN in the mixtures. Since the calculations involve thermodynamics exclusively, neither reaction rate nor the physical properties of the mixtures are addressed.

*Aldrich Chemical Company, Milwaukee, WI

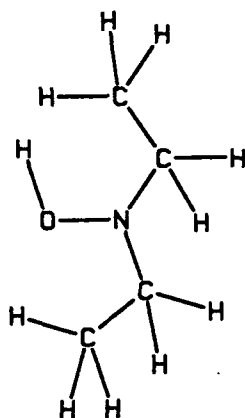


Figure 5. N,N-diethylhydroxylamine (DEHA).

Table 1. Potential HAN-TEAN-DEHAN Mixtures

Propellant	HAN	TEAN	DEHAN	Impetus	Flame Temperature
	(Weight-Percent)			(J/g)	(K)
4600	60.81	19.19	0.00	900.8	2,476
4605	60.81	18.23	0.96	903.6	2,482
4610	60.81	17.26	1.93	906.5	2,489
4620	60.80	15.35	3.85	912.3	2,503
4640	60.79	11.50	7.71	923.7	2,530
4680	60.77	3.84	15.39	946.4	2,583
9800	60.76	0.00	19.24	957.7	2,609

HAN and TEAN (Thiokol Lots 851-47 and 280) were concentrated to 93.15 and 80.23 weight-percent, respectively, by water stripping at 50° C under vacuum and together with the DEHAN mentioned earlier, were used to prepare 1 kg of each of the propellant mixtures described in Table 1. The concentration of the three salt solutions and of the propellant mixtures was determined titrimetrically (Sassé 1990). The density of the formulated mixtures was determined at 20° C and was used to calculate molarity and volumetric impetus since the propellants are normally metered into various test fixtures by volume rather than by weight. Density and volumetric impetus data are presented in Table 2. It would be expected that removal of TEAN will reduce the extensive hydrogen-bonding promoted by its OH groups, and thus diminish many of the desirable physical properties characteristic of the HAN-TEAN propellant mixtures.

Table 2. Density and Volumetric Impetus of the HAN-TEAN-DEHAN Mixtures

Propellant	Density (g/ml)	Volumetric Impetus (J/ml)
4600	1.4442	1,300.9
4605	1.4409	1,302.2
4610	1.4387	1,304.2
4620	1.4349	1,309.1
4640	1.4277	1,318.8
4680	1.4112	1,335.6
9800	1.4035	1,344.1

The density data clearly support this expectation and many of the colligative and transport properties of the propellants should exhibit similar trends (Klein 1990). The glass transition temperature of the mixtures containing DEHAN should be higher than that of LGP1846 and viscosity should show greater variation with temperature. The effect of compositional variation on volumetric impetus is less severe than on gravimetric impetus because density decreases as DEHAN replaces TEAN, but the effect is not wholly removed. The molar composition of the mixtures is given in Table 3. Since reaction initiation temperature decreases with increasing nitrate concentration (Sassé and Klein 1979), one would predict that commencement of reaction will be observed at a lower temperature as DEHAN replaces TEAN. However, the effect is small enough (8°/mole) that the 1.6° change expected at the composition extremes should be within the experimental uncertainty of its measurement. Although the water content of the mixtures is constant by weight, a decrease by volume is seen.

Reaction initiation, ignition, and combustion of the mixtures was evaluated using an accelerating rate calorimeter (ARC) that had been modified for LP studies (Klein and Leveritt 1989). Sample volume was 30 μ l in all cases so that impetus varied as shown in Table 2. All reaction studies were carried out at a nitrogen pressure of 3.9–4.0 MPa in order to obtain complete combustion after reaction initiation. Reaction initiation was observed over the temperature range 113–125° C. Initiation temperature does not correlate with sample composition, and the reaction initiation temperature range is small enough to be accounted for as sample-to-sample variation.

Table 3. Molarity of the HAN-TEAN-DEHAN Mixtures

Propellant	Concentration (Moles/liter)				Total Nitrate
	HAN	TEAN	DEHAN	Water	
4600	9.15	1.31	0.00	16.05	10.46
4605	9.13	1.24	0.09	16.01	10.46
4610	9.11	1.17	0.18	15.99	10.47
4620	9.09	1.04	0.36	15.95	10.49
4640	9.04	0.77	0.74	15.86	10.54
4680	8.93	0.23	1.43	15.68	10.62
9800	8.88	0.00	1.78	15.56	10.66

Gas generation associated with the ignition-combustion event was recorded on a Nicolet Model 4096 digital oscilloscope* and converted to pressure vs. time using appropriate calibration constants. An example of such data for propellants 4600 and 9800 is shown in Figure 6. The amplitude of the 9800 record is normalized to 4600 by division of the data by 1.033, the 9800:4600 volumetric impetus ratio. Both samples burned essentially to completion leaving no measurable residue other than water. The oscillations seen in the cooling portion of the 9800 pressure record are the result of a ringing induced in the pressure gauge by the rapid pressure rise (organ pipe effect). Similar traces were obtained for all of the samples tested. In every case, the start of the trace (time = 0) is taken as the first point that is 0.629 kPa above the baseline, the trigger level of the oscilloscope.

3. DISCUSSION

It will be assumed, for discussion purposes, that gas generation rates in the ARC and propellant burning rates are directly related. The validity of this assumption is supported by observation of rapid heat evolution that coincides with gas generation and the fact that no further exothermic activity is detected after the event recorded in Figure 6. Only combustion products are found in the ARC bomblet after conclusion of the experiment. Although it is reasonable to suggest that the events recorded in Figure 6

*Nicolet Instrument Corp., Madison, WI

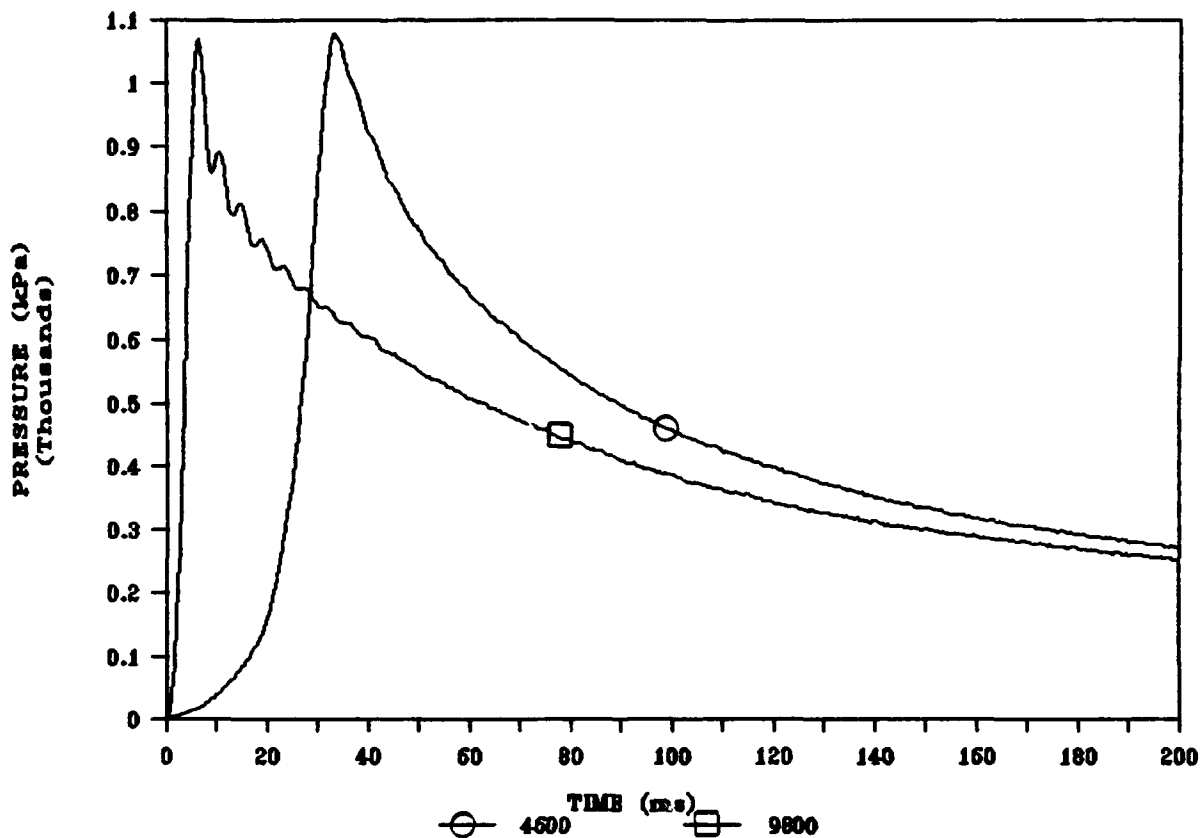


Figure 6. Gas Production From the Combustion of Propellants 4600 and 9800.

are associated with combustion of the propellant sample, the specific relation between gas generation rates and burning rates is not known. It will be further assumed that this relationship is the same for all of the propellants investigated because of the similarity in sample composition and properties, and the replicated experimental conditions employed.

The portion of the pressure traces that is of interest in this study is the segment from onset of gas generation to some value near the maximum pressure. The portion of the 4600 data of Figure 6 from the onset of gas generation to 700 kPa is shown in Figure 7. Included in the figure is the curve generated by the equation $P = At^B$ where P is pressure (kPa), t is time (ms), and A and B are the constants 0.55 and 2.66, respectively. The goodness-of-fit of the power law equation to the experimental data, seen in

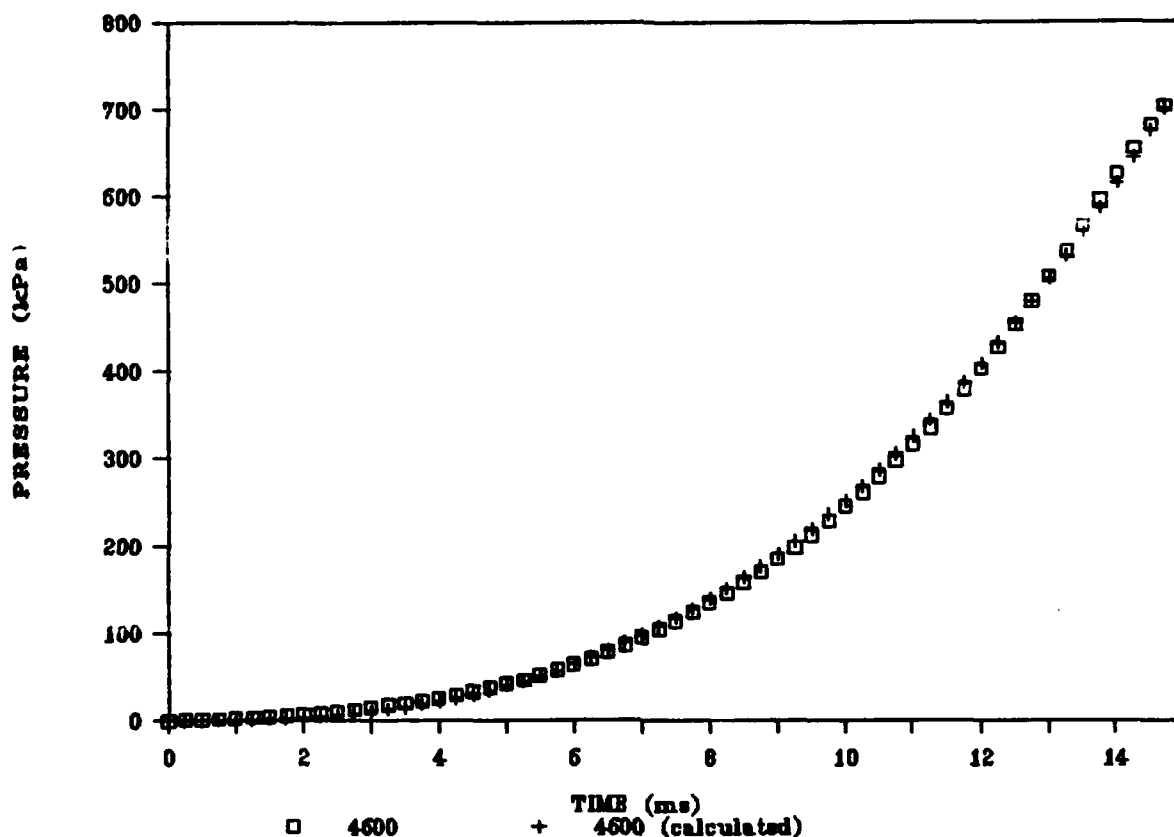


Figure 7. Gas Generation, Propellant 4600.

Figure 7, is representative of the results obtained for all of the propellants listed in Table 1. Although the most precise duplication of the experimental data is obtained by selection of appropriate values for both A and B, an adequate fit is obtained if B is held constant. Selection of values of A to obtain best fit to the experimental data is equivalent to multiplication of the propellant 4600 experimental data shown in Figure 7 by a constant, thus creating a gas generation rate scaling factor normalized to propellant 4600. These scaling factors are listed in Table 4. The highest gas generation rates were obtained with propellant 9800. If it is assumed that gas generation by the HAN-TEAN component of the ternary HAN-TEAN-DEHAN mixtures proceeds independently of the HAN-DEHAN component, then gas generation rates can be calculated according to the weight fraction of DEHAN in the mixture, that is:

$$\text{Normalized Rate} = 1 (\text{wt frac TEAN}) + 17 (\text{wt frac DEHAN}) [3].$$

The calculated values thus obtained are included in Table 4.

Table 4. Gas Generation Rate for the HAN-TEAN-DEHAN Mixtures

Propellant	Gas Generation Rate (Normalized to 4600)	Calculated Rate (Eq. [3])
4600	1.0	1.00
4605	1.5	1.80
4610	3.9	2.60
4620	5.5	4.20
4640	6.0	7.40
4680	14.5	13.80
9800	17.0	17.00

The agreement between normalized rates and the calculated values is rather good and is shown in Figure 8.

The fact that the observed increase in gas generation rate parallels the increased volumetric impetus of the mixtures warrants comment. It is certainly reasonable to suppose that burning rate is a function of the energy content of the propellant mixtures and the data provide an opportunity to evaluate the contribution of reaction kinetics to the overall energy release observed. The propellant mixtures LGP1845 and LGP1846 both contain only HAN and TEAN. The lower water content and higher density of LGP1845 results in a volumetric impetus of 1,387 J/ml, a value well in excess of the volumetric impetus of mixture 9800. However, the observed gas generation rate of LGP1845 is lower than that observed for 4680 and 9800 and, in contrast to the DEHAN containing mixtures, fitting its gas generation rate to $P = At^B$ requires that the values of both A and B be different from those used for LGP1846. Thus, it would appear that the combustion chemistry of the propellant mixture plays an important role in establishing the rate of energy release and simply increasing the energy content of the propellant is not a viable method for achieving this end.

The two-dimensional, oscillation producing model was run for each of the cases above, using the appropriate impetus, density, and pre-exponential multiplier. Figure 9 compares the chamber pressure obtained at the wall from three of the calculations. The propellant 4620 data are shifted downward 100 MPa and the propellant 9800 data are shifted downward 200 MPa to permit comparison. As burning

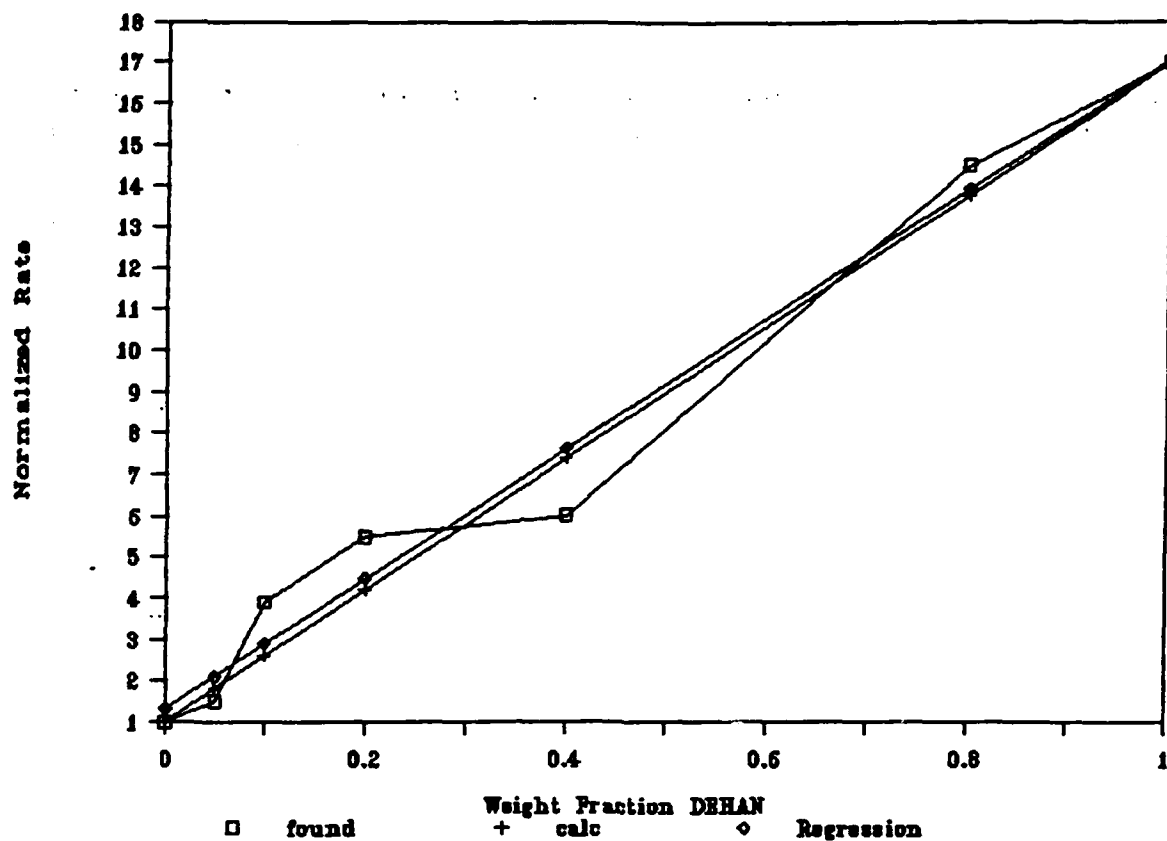


Figure 8. Normalized Gas Generation Rates as a Function of DEHAN Weight Fraction.

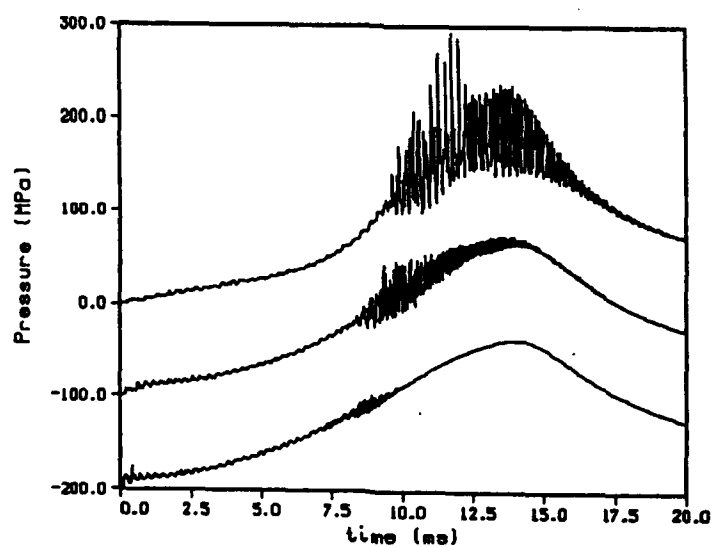


Figure 9. Model Chamber Pressures. 4600 (Top). 4620 (Middle). 9800 (Bottom).

rate increases, the oscillations begin earlier but are much smaller in amplitude. These results can be explained qualitatively by considering that local generation of gas occurs sooner in the faster burning propellants, but the dependence of burning rate on pressure is the same for all of the mixtures. As a result, the portion of the oscillations that is caused by the B term in AP^B will appear sooner. However, faster burning inhibits accumulation of unburned propellant in the combustion chamber so that both the amplitude and duration of the oscillations are reduced. Since an increase in burning rate affects the time that the onset of oscillations are seen, it was of considerable interest to determine whether the frequencies associated with these oscillations also changed. Fourier transforms of the oscillations were obtained at their start, at their peak, and in a fixed 1-ms time window, 11 ms after the start of injection (this latter case duplicating Figure 3). No significant differences are seen between these data sets. Figures 10a and 10b show the Fourier transforms of the entire set of formulations for the third case considered. The overtones at lower frequency disappear quickly as DEHAN replaces TEAN in the formulation, but a 21-kHz signal increases to a maximum with propellant 4620. This overtone is the last to die out. Whether or not these findings are artifacts of the model is not yet known.

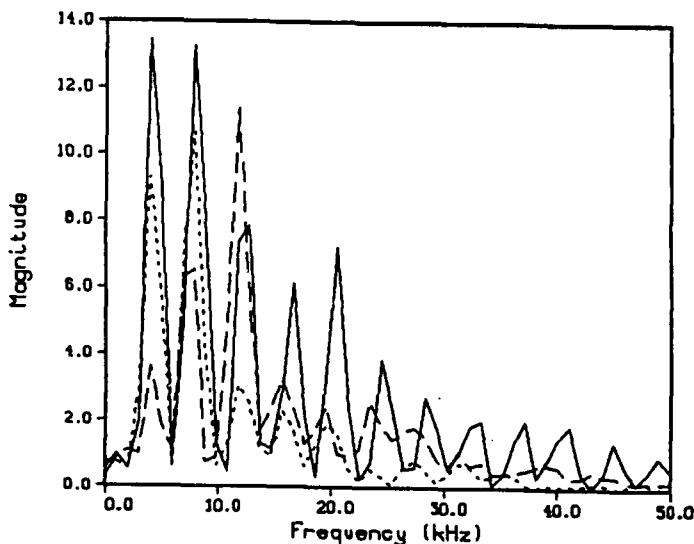


Figure 10a. Fourier Transforms - 11-12 ms.
4600 (Line), 4605 (Dot), 4610 (Dash).

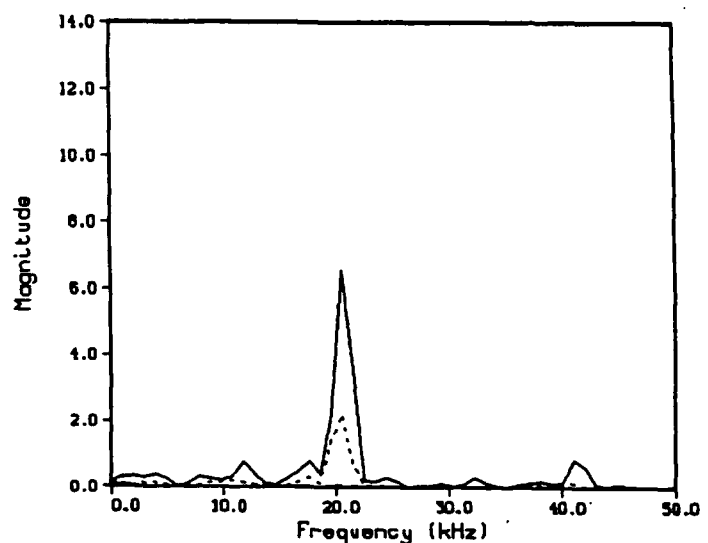


Figure 10b. Fourier Transforms - 11-12 ms.
4620 (Line), 4640 (Dot), 4680 (Dash),
9800 (Dot-dash).

4. CONCLUSIONS AND FUTURE WORK

Based on the limited work to date, it is reasonable to conclude that increasing the propellant burning rate may reduce the amplitude and frequency of the pressure oscillations seen in LPGs. Although conditions in the ARC are very much removed from those in the gun or in more realistic gun simulators, the data indicate that there is sufficient promise in the approach to warrant further investigation. A reasonable next step would be to use the formulated propellant mixtures in a small injector/combustor in which pressure oscillations have been seen, such as the test fixture at the Combustion Research Facility, Sandia National Laboratory, Livermore, CA (Carling, Rychnovsky, and Griffiths 1989). If it can be demonstrated that pressure oscillations in gun simulators are dependent on propellant burning rate, gun designers might be able to increase gas generation rate by mechanical modifications, having already shown (DeSpirito et al. 1991) that jet flow dispersers reduce low-frequency oscillations.

It should be pointed out that an increase in propellant burning rate by replacing some or all of the TEAN with DEHAN can be the source of a number of problems in a LPG system. Replacement of a significant portion of the TEAN with DEHAN would be expected to adversely change some of the physical properties of the mixture. Although toxicity and handling characteristics should not be markedly affected, the vulnerability of propellant to incidental attack may be enhanced. Since burning will presumably begin closer to the injector orifice, the possibility of flame propagation back through the injector orifice to the propellant reservoir must be considered. It is reasonable to expect that burning in closer proximity to the orifice exit will change the pressure gradient across the injector and thereby decrease propellant injection rate. This, in turn, could be the source of several problems such as cavitation, boundary layer separation, and flashback into the propellant reservoir, all of which will adversely affect gun performance. It should also be noted that although burning rate increases, thermal initiation temperature is essentially the same for all of the propellant mixtures being discussed. Heat transport by conduction or convection relies primarily on the ability of the gaseous products of combustion to transfer heat to the fresh propellant being injected. Since the quantity of heat needed to start reaction is the same for all of the mixtures, and the combustion products are compositionally the same, little or no difference should be seen other than those that would result from the closer proximity of the burning propellant to the orifice. The propellants are, however, relatively transparent so that radiation may be a significant mode of energy transfer. If combustion closer to the injector orifice provides enhanced line-of-sight to the propellant reservoir, then energy transfer via radiation could become important. It is reasonable to assume that modification of propellant burning rate will require some redesign of the propellant injector. Quite possibly, a combination of mechanical and chemical modifications will be required to either eliminate or significantly reduce the oscillations currently observed.

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